

Water repellency effects on the pore structure of wetland soils

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Abstract

Soil organic matter induces water repellency during drying and promotes structure recovery after rewetting, yet how these processes interact remains unclear in wetland soils. Here we show, for topsoil and subsoil from 13 Chilean wetlands (38–54°S), that water repellency increases exponentially with drying intensity at both depths, water drop penetration times rising from under 7 s at saturation to 39–72 s. Recovery diverges with depth, and repellency and pore structure do not recover independently: the topsoil regains both wettability and pore volume within days, whereas the subsoil retains persistent repellency and a pore volume still 28% below initial after five days of rewetting. We interpret this coupled asymmetry through an analogue of preconsolidation in soil mechanics: drying within a soil's historical range of matric potentials, as in the topsoil, is largely reversible, whereas drying beyond it, as in the groundwater-buffered subsoil, produces a poorly reversible, "virgin" response. The framework predicts elastic behaviour on re-exposure, as re-drying rather than virgin drying. Organic carbon quantity explains most of this variation, accounting for 67% of the variance in contact angle; compositional indices add nothing independent. Recognising this coupling, and the drying history governing it, offers a transferable criterion for anticipating irreversible wetland change.

Highlights

Drying increased soil water repellency in wetlands by up to twenty-fold.

Topsoil regained both wettability and pore volume; subsoil regained neither.

Organic carbon quantity explained most variation in both processes.

Wetland subsoils are vulnerable to irreversible change under future drying.

INTRODUCTION

Wetland ecosystems in the arid and semi-arid regions of Chile are particularly vulnerable to climate change, as the country is projected to be strongly affected by declining precipitation and increasing soil desiccation [1]. Across the latitudinal range studied here the two components of this drying signal differ in strength: end-of-century projections indicate robust precipitation reductions of 10–30% for Northern Patagonia but no consistent precipitation trend for Southern Patagonia, whereas near-surface warming of up to 4°C is projected with high inter-model agreement across both subregions [1]. Rising atmospheric water demand may therefore drive soil drying as strongly as declining rainfall, and this shift is already measurable: the Patagonian steppe has recorded increasing atmospheric water demand alongside declining water supply, a combination interpreted as a transition from episodic drought towards persistent aridification, in which drying exceeds the resilience of the system and produces permanent change [2]. These ecosystems, locally known as Vegas or Mallines, cover approximately 29,200 km², about 4% of Austral Patagonia [3], [4]. They sustain more than half of Chile's national sheep population by providing critical forage for rural communities from southern Chile to Austral Patagonia

[5]. Despite this limited extent, well-preserved Vegas store up to 300 Mg C ha⁻¹ and hold on average 8,500 m³ of water ha⁻¹ in the upper two meters, making them disproportionately important for regional carbon and water regulation [6]. Vegas soils are commonly associated with Histosols or peatlands [7], although Luvisols, Cambisols, and Gleysols have also been reported, typically sustained by winter groundwater recharge derived from high-mountain snowmelt [8], [9], [10].

Although wetlands occupy only 4–8% of the Earth's terrestrial surface [11], they represent a globally significant terrestrial carbon reservoir [12], and an important regional freshwater resource [13]. Peatlands alone hold approximately 10% of global freshwater and account for 20–30% of global soil organic carbon [14]. Current literature suggests that organic matter content [15], plant species composition [16], and soil moisture status are key factors influencing wetland soil water repellency [17]. This moisture dependence is attributed to the coating of soil particles and aggregates by partially hydrophobic soil organic matter (SOM) [18]. These amphiphilic molecules contain hydrophilic C = O groups and hydrophobic CH groups [19]. Under moist conditions, hydrophilic groups tend to orient outward, whereas prolonged exposure to critically low water contents promotes molecular reorientation, exposing hydrophobic groups at the particle surface [19].

Soil hydrophobicity, or soil water repellency, has important consequences for peatland (i.e., highly organic wetland soils) hydrological functioning. It can reduce infiltration, thereby limiting plant establishment and slowing vegetation recovery, while also increasing overland flow, runoff generation, and erosion risk [17], [20]. Similarly, extreme hydrophobicity can affect the capillary rise of water [21], which is particularly detrimental in wetlands due to their dependence on groundwater [9]. Drying does not only alter wettability; it also changes soil volume, and in organic soils this change is large and only partly reversible. Fibrous peat can lose up to half of its volume upon air drying, and whereas clayey soils recover 74–90% of the lost volume upon rewetting, organic soils recover only 22–23% [22], [23]. Even natural seasonal cycles can shift pore volume measurably: [24] reported 5% porosity changes between summer and winter in southern Chilean soils as a consequence of wetting and drying alone. Critically, shrinkage and hydrophobicity are not independent. The hysteresis between shrinkage and swelling has been attributed to the formation of water-repellent films on particle surfaces, to pore-geometry effects, and to rearrangement of the pore system during shrinkage itself [25], so that repellency both accompanies and impedes the recovery of pore volume. Whether that recovery occurs depends on the hydraulic history of the soil: pore size distribution and shrinkage capacity are strongly modified once the maximum pre-drying stress previously experienced is exceeded [22], and shrinkage capacity has already been shown to vary systematically among Patagonian Vega soil types [6], [8]. For wetland soils this combination is particularly damaging. A pore system that does not regain its volume permanently retains less water, eroding the buffering capacity these ecosystems provide during dry periods; and the air that replaces that water exposes organic carbon accumulated over millennia to oxidation, potentially accelerating its mineralization. Both effects act in the same direction, and neither reverse when the rain returns. Research explicitly addressing capillary rise under water-repellent conditions in groundwater-dependent wetlands nevertheless remains scarce, and that study is among the first to quantify these dynamics in Patagonian Vegas.

These hydrological effects of hydrophobicity may also influence soil physical resilience. The resilience concept originates in ecology, where it was defined as the capacity of a system to absorb disturbance while retaining its fundamental structure and function [26]; applied to soils, this translates into the capacity of a soil function (e.g., water retention) to recover over time after disturbance [27]. Soil resilience has been evaluated using indicators such as the water retention curve [28], soil structural stability [29], and microbial properties [30] under different forms of stress, including mechanical, chemical, and hydraulic stress [28], [31]. In the case of hydraulic stress, this typically involves exposing the soil to different levels of drying. The soil physical resilience can be evaluated through the recovery of the void ratio over time [32]. Other authors [33] indicate that not only is the recovery of soil volume (as captured by the void ratio) relevant, but also the recovery of soil functionality (e.g., evaluated by air conductivity).

It is well-known that soils with greater SOM tend to exhibit greater capacity to recover soil physical functions [32], [34]. That evidence, however, comes from mineral soils, in which organic carbon rarely exceeds a few percent. Wetland soils operate in an entirely different range: across the sites studied here, total organic carbon spanned 3.7–44.0% in the topsoil and 1.1–48.8% in the subsoil, an order of magnitude above typical mineral soils. Whether relationships established at low organic carbon contents extrapolate to this range is therefore an open question. Soil organic matter improves soil resilience; however, at the same time, SOM induces hydrophobicity when soils dry out. Therefore, it remains unclear whether the positive effect of SOM on resilience outweighs its role in inducing hydrophobicity as the soil dries. Some authors have found a relationship between resilience and hydrophobicity at the aggregate level, since water repellency would prevent aggregate slaking by promoting their slow re-wetting [35].

Conversely, the effect of organic matter on soil hydrological and physical function is not always positive. A global meta-analysis found that its influence on plant-available water storage is often smaller than commonly assumed [36], and numerical modelling has shown that organic-matter-driven increases in shallow water retention can raise near-surface evaporation, thereby reducing the water actually available to plants and to recharge [37].

We hypothesize that soil organic matter jointly controls water repellency and physical resilience primarily through its quantity, rather than through a direct causal link between the two processes, and that structural and functional recovery will be greater in the topsoil than in the subsoil because the applied drying stress falls within the topsoil's historical range of field matric potentials but exceeds it in the subsoil.

Given this background the present work aims to: i) evaluate the hydrophobicity and resilience of wetland soils in arid and semi-arid ecosystems, and ii) determine how both processes relate to soil physicochemical properties such as organic carbon content, bulk density, and texture, to improve our understanding of these poorly studied interactions. A better comprehension of these mechanisms is pivotal for conserving the hydrological and biogeochemical functions of wetlands, which in turn underpin the productive and ecological value these ecosystems provide to Patagonian rangelands.

RESULTS

Water Repellency

In the sample of the topsoil layer, WDPT increased exponentially with drying intensity under both treatments, reaching strong hydrophobic levels (> 60 s) at -15350 hPa (Fig. 3A). After rewetting, WDPT returned to a narrow range (2.5–5.7 s) under both drying treatments, with no credible evidence of a difference from pre-drying values, indicating that repellency generated by drying was largely reversible indicating fast molecular relaxation in the topsoil samples (Fig. 3B).

In the subsoil samples, WDPT followed a similar exponential increase with drying intensity but remained consistently higher than in topsoil across most of the pF range ($pF = \log_{10}$ of the matric potential expressed in hPa), with rewetting proceeding more slowly, nearly reaching hydrophobic levels (> 60 s) at -15350 hPa (Fig. 3C). WDPT after rewetting of subsoil remained elevated relative to pre-drying values under both treatments (8.1–14.6 s at -500 hPa; 10.1–19.8 s under -15350 hPa), with the largest values and greatest variability occurring shortly after rewetting began and progressively declining over subsequent recovery days, indicating that repellency generated during drying did not fully reverse in the subsoil (Fig. 3D).

Contact angle of air-dried soil was greater in the topsoil than subsoil, with several observations approaching or exceeding the 90° threshold. The subsoil had more variable contact angle, with most observations below 90° . Overall, these results indicate depth-dependent wettability, with more consistent hydrophobicity in the topsoil and more variable hydrophobicity in the subsoil (Fig. 4).

Void Ratio and Air Conductivity

In the topsoil (Fig. 5A), void ratio declined significantly for either drying treatment and increased progressively during recovery. Under sDS, we found no credible evidence of a difference in void ratio from the initial state by the fifth recovery day, whereas under mDS it remained significantly below the initial condition through the fourth and final recovery day.

In the subsoil (Fig. 5B), the stress-induced decline to void ratio was much larger under sDS (-1.75) than under mDS (-0.37), and recovery was only partial under both treatments, remaining significantly below the initial state at every stage.

Air conductivity (kl) followed a similar depth-dependent pattern (Fig. 6). In topsoil, kl increased significantly under drying stress regardless of its severity ($\sim 62\%$ under sDS) and returned to values for which we found no credible evidence of a difference from the initial state by the end of recovery, and no credible evidence of a difference between mDS and sDS at any stage. In subsoil, kl also increased significantly during stress ($+68\%$ under mDS, $+77\%$ under sDS), but recovery was incomplete under sDS,

which remained significantly different from the initial state; kl was significantly greater under mDS than under sDS throughout the experiment.

Relationship Between Soil Water Repellency, Void Ratio and Air Conductivity

After establishing depth-dependent patterns on hydrophobicity and porosity individually, it was examined how hydrophobicity and resilience indicators related to one another. The hydrophobicity index (HI), which represents the decline in the water drop penetration time (WDPT) per unit of volumetric water content, showed only a weak, exploratory relationship with the resilience index (RI) (Fig. 7A; linear model, $R^2 = 0.079$, $p = 0.045$), and is presented here mainly to illustrate the limited predictive power of static moisture-slope indices relative to the much stronger relationships found for contact angle and bulk density (see below).

Contact angle (CA), used as a direct indicator of soil surface hydrophobicity, was positively associated with the recovery slope (RS) following an exponential model (Fig. 7B; $R^2 = 0.197$, $p = 0.01$).

The strongest relationship was observed between the two-resilience index themselves (Fig. 7C), where RI and RS were positively and significantly related under a linear model ($R^2 = 0.544$, $p < 0.01$).

Considering only significant relationships, the recovery slope RS, was significantly related to BD (Fig. 8A), ^{13}C (Fig. 8B), C:N ratio (Fig. 8C), CH_h/CO_h ratio (Fig. 8D), and total organic carbon (TOC, Fig. 8E). RS increased logarithmically with C:N ratio ($R^2 = 0.093$, $p = 0.035$), although this relationship was weak. In contrast, RS declined exponentially with increasing BD ($R^2 = 0.352$, $p < 0.01$). RS increased exponentially with TOC ($R^2 = 0.269$, $p < 0.001$) and with ^{13}C ($R^2 = 0.217$, $p < 0.01$). RS increased logarithmically with the CH_h/CO_h ratio ($R^2 = 0.216$, $p < 0.01$).

Contact angle was strongly related to BD (Fig. 8F), ^{13}C (Fig. 8G), CH_h/CO_h ratio (Fig. 8H) and total organic carbon (TOC, Fig. 8I), through logarithmic models. CA decreased with increasing BD ($R^2 = 0.610$, $p < 0.01$), and increased with TOC ($R^2 = 0.666$, $p < 0.01$), ^{13}C ($R^2 = 0.764$, $p < 0.01$), and CH_h/CO_h ratio ($R^2 = 0.475$, $p < 0.01$).

The first two principal components explained 79.1% of the total variance, with Dim1 accounting for 58.0% and Dim2 for 21.1% (Fig. 9). Dim1 represented a gradient separating soils with higher bulk density (BD), which loaded negatively on the axis, from soils characterized by greater cation exchange capacity (CEC), total organic carbon (TOC), ^{13}C abundance, and stronger hydrophobicity indicators such as CH_h/CO_h and CA, which loaded positively; the recovery slope (RS) also loaded positively on this axis, linking structural resilience to the same organic matter gradient.

Dim2 was primarily associated with pH and ^{15}N , which loaded positively, and with RS and CH_h/CO_h , which loaded negatively, representing variation largely independent of the dominant organic matter axis.

Although RI was excluded from this ordination due to low individual sampling adequacy, its strong bivariate relationship with RS (Fig. 7C, $R^2 = 0.544$) is consistent with the pattern captured by Dim1.

DISCUSSION

Wetland soils sampled across Chile had markedly increased soil water repellency with drying severity, becoming most pronounced at the wilting point of -15350 hPa. The major driver of water repellency was soil organic matter, topsoils had greater water repellency than subsoils. There was recovery capacity after removing the hydraulic stress in topsoils, but it was slower for subsoil. Drying also induced shrinkage of the soils that did not fully recover upon rewetting. Like water repellency, the recovery with rewetting was poorer in the subsoil, presenting a potential risk to water recharge following dry periods for these soils [9]. As this study had sites spanning a latitudinal gradient of nearly 2000 km, it captures broad geographic differences across Chile. With the exception of two sites that are Sphagnum peatlands, the remainder were located in arid or semi-arid areas and were managed for livestock, further supporting the representativeness of the results.

Water repellency under different drying intensities in surface and subsurface layers

The exponential increase in WDPT with drying at both depths confirms that soil moisture is the principal factor controlling repellency development [16], with severe drying (sDS) promoting substantially greater repellency than moderate drying (mDS), as also reported by [38], [39] in a wide variety of soil types.

However, rewetted responses contrasted between depths. Topsoil repellency proved largely reversible, consistent with rapid molecular relaxation of the amphiphilic organic coatings once water becomes available, whereas in the subsoil it persisted. Both depths therefore developed repellency during drying, but only the subsoil retained it after rewetting. This depth-dependent persistence mirrors the differential soil structure resilience discussed below and is consistent with the subsoil undergoing a drying event beyond its historical range (see section Resilience of the soil pore system, below). The contact angle data add further insights to this picture. Contrary to the WDPT pattern, intrinsic wettability was lower in the subsoil, which showed a median contact angle of 55° compared with 110° in the topsoil, consistent with its lower organic carbon content. This apparent divergence is informative rather than contradictory: contact angle was measured on air-dried, disturbed material and therefore reflects the intrinsic wettability of the soil matrix, whereas WDPT was measured on intact cores after stress and rewetting and therefore integrates structure and drying history. That the subsoil is intrinsically less hydrophobic yet retains more persistent repellency in intact cores reinforces the interpretation that its behaviour is governed by structural and historical factors rather than by organic matter chemistry alone. The subsoil was nonetheless accompanied by a higher CHh/COh ratio (orange dots in Fig. 8, D and H); however, the multivariate analysis presented below shows that this compositional index closely tracks total organic carbon rather than acting as an independent driver of hydrophobicity, so the pattern observed here is

better interpreted as reflecting organic matter abundance rather than a distinct depth-related shift in aliphatic group prevalence, which would otherwise be expected to decline with depth as aliphatic C–H compounds degrade more rapidly than other SOM fractions [40].

Resilience of the soil pore structure under two drying intensities

When assessing resilience, the subsoil also stands out. This depth never fully recovers its void ratio after a dessication (hydraulic stress), but more importantly, it loses more than half of its pore volume during hydraulic stress and does not recover it after five days, indicating the subsoil's low resilience. The apparent full recovery of the topsoil under the severe treatment should not be over-interpreted: its mean recovery deficit was larger than under moderate drying (13% versus 3%), but so variable among sites that it lost statistical significance. This is consistent with the studies by [41], [42], [43] on different types of wetland soils. [41] explain that this inability to recover its previous volume is because the maximum historical drying level ever experienced by these soils was exceeded (which is consistent with the fact that wetland soils are normally saturated); therefore, following that drying event, a new soil structure develops, reflected in an altered pore volume.

This behavior parallels the concept of a virgin compression line in soil mechanics, where a soil subjected to a stress exceeding its historical maximum (preconsolidation stress) undergoes large, largely irreversible deformation, whereas subsequent loading within the previously experienced stress range produces a much smaller, largely elastic response [44]. Applying this framework to matric suction rather than mechanical load – a cross-disciplinary link for which a formal theoretical basis exists, since coarse pores collapse first under mechanical stress in much the same way as they drain first under hydraulic stress during drying [45] – the topsoil is routinely exposed to atmospheric wetting-drying cycles in the field and had therefore likely already experienced matric potentials comparable to or more negative than those imposed here; the laboratory treatments thus represent a re-drying (rehydrophobisation) event within its existing soil structure and hydrophobic history, consistent with its high resilience and largely reversible repellency. In contrast, the subsoil remains close to permanent saturation under current field conditions, buffered by its proximity to the water table, and the severe treatment applied here plausibly exceeded any suction it had previously experienced.

This is consistent with the position of the water table close to the subsoil depth: on the pF scale, the applied matric potentials correspond to equivalent capillary rise heights of approximately 4.9 m (mDS) and 151 m (sDS) above a free water table, both far exceeding the shallow water table typically sustaining this depth under field conditions. These two treatments therefore serve different purposes: the moderate stress (mDS) approximates a plausible drying scenario under a declining water table, whereas the severe stress (sDS) is better understood as a deliberately extreme boundary condition used to locate the threshold beyond which structural change becomes poorly reversible, rather than as a simulation of any expected field state. Importantly, the subsoil failed to recover its initial void ratio under both treatments – the deficit reached 4% under mDS and 28% under sDS – so the conclusion that this depth is

structurally vulnerable to drying does not rest on the severity of sDS alone. In a companion study of a comparable Patagonian wetland, [9] documented a progressive decline in water table height over a two-year monitoring period and noted that the organic-rich center of the meadow showed incomplete apparent saturation at depth, tentatively attributed in part to a water-repellency effect – a pattern consistent with the persistent, poorly reversible hydrophobicity reported here for the subsoil. A virgin drying event of this kind would be expected to produce comparatively large, poorly reversible structural collapse and a more persistent, primary hydrophobicity, consistent with the incomplete recovery of void ratio and air conductivity and with the elevated post-rewetting WDPT observed in this depth. This framework generates a testable prediction: a second exposure of subsoil samples to the same severe suction should behave more like a re-drying event, with markedly improved reversibility of both structure and repellency, analogous to the stiffer response typically observed on reloading within a soil's stress history.

Considering the functioning of the porous system, air conductivity (kl) increased during the stress stage at both depths and both treatments due to the increase in air-filled porosity [8]. In the topsoil, kl increased under sDS by approximately 62% from the initial to stress stage, then returned to a value for which we found no credible evidence of a difference from the initial state during recovery. This agrees with the high resilience observed in void ratio. In the subsoil, kl also increased during stress under mDS (+ 68%) and sDS (+ 77%). However, after sDS, the recovery value tended to remain below the initial state, although this difference was only marginally significant and sensitive to the choice of statistical test ($p = 0.04\text{--}0.07$). Therefore, the functional indicator (kl) supported the soil structure indicator (void ratio): the topsoil showed strong recovery, whereas the subsoil under severe drying showed persistent alteration after rewetting. This persistent increase in aeration has a potential biogeochemical consequence: organic carbon that accumulated under near-permanent saturation would become exposed to oxygen, and its mineralisation could accelerate. Our experiment was not designed to capture this process, since 48 days of drying is far shorter than the timescale over which such carbon losses operate, but the structural change we document provides the physical precondition for it.

As shown in this study, the persistent hydrophobicity and incomplete soil physical recovery of the subsoil are significant in light of a future climate characterized by lower rainfall and periods of higher temperatures and drier conditions, such as those expected for Chile and other parts of the world [1], [46]. Currently, the subsoil at all sampled sites remains close to the interface between the saturated and unsaturated zones, which limits hydrophobicity due to its consistently high soil moisture. In the future, however, a dropping water table may promote soil drying, increasing water repellency and making re-wetting of the subsoil increasingly difficult, implying a negative feedback loop. On one hand, this could allow oxygenation of sites where recalcitrant carbon currently remains protected in its organic form [47], [48]. On the other hand, hydrophobicity itself may paradoxically help preserve this carbon: although the most significant process for carbon sequestration is the inability of carbon to decompose rapidly due to a fluctuating water table [49], it cannot be ruled out that hydrophobicity also promotes carbon sequestration by limiting rewetting and, consequently, the microbial decomposition activity that depends on it [50].

Relationship between soil physical resilience and water repellency

Beyond this shared dependence on drying history, hydrophobicity and resilience are also connected through organic matter itself. A higher organic matter content is associated with greater hydrophobicity [51] and, in the same context, is thought to promote greater physical resilience [32]. Both relationships are confirmed in this study, either through total organic matter levels or through some of its components, such as ^{13}C or the C:N ratio. However, when directly testing the relationship between hydrophobicity and resilience indices, one must be cautious in drawing conclusions. RI, which quantifies the proportion of pore volume recovered after stress, increased slightly with increasing HI, indicating that soils in which repellency changed more strongly during rewetting tended to exhibit somewhat greater final structural recovery. However, the low coefficient of determination indicates that HI explained only a small fraction of the variability in RI.

In contrast, the relationship between RS (which represents the rate of void ratio recovery during the post-stress phase), and CA indicates that soils with higher contact angles tended to recover pore volume more rapidly. Although statistically significant, the explained variance remained moderate, suggesting that additional factors also influenced recovery rates. This apparent tension can be resolved through two non-exclusive mechanisms. First, both CA and RS may be jointly driven by a common underlying factor, total organic carbon, rather than one causing the other: a multiple regression of CA on CHh/COh, TOC, and clay content (Supplementary Table S2) shows that once TOC is accounted for, CHh/COh no longer explains additional variance in CA ($p = 0.155$), while TOC remains highly significant ($p < 0.01$); TOC and ^{13}C are themselves strongly collinear ($r = 0.977$), indicating that these variables largely capture a single dominant axis of organic matter abundance rather than several independent lines of evidence. Second, and consistent with the aggregate-level mechanism proposed by [35], moderate hydrophobicity may slow the rate of water entry during rewetting enough to prevent abrupt slaking and the associated collapse of macropores, thereby preserving more of the pre-stress pore architecture and allowing faster subsequent recovery. The present dataset cannot fully separate these two mechanisms, and we do not interpret CA as a direct causal driver of resilience; rather, both hydrophobicity and resilience appear to be co-expressions of organic matter quantity, occasionally reinforced by a kinetic protective effect during rewetting.

The comparatively weak performance of HI in particular may reflect that resilience of the porous system after dehydration depends on a large number of interlinked variables, including physical processes such as drying intensity and history [41], and other variables such as the quantity and quality of organic matter and pH [52]. It is therefore difficult to create an index or indicator that captures all these processes and correlates them with hydrophobicity. In an attempt to capture the variability in water repellency resulting from soil moisture, an HI was created; however, this did not correlate well with the water repellency indices. An example of this is found in the subsoil, which exhibits lower re-wetting after mDS and sDS, yet contains a lower amount of organic carbon (Supplementary table S2). This suggests that the capacity for re-wetting (i.e., resilience) is governed by processes dependent on soil structure [53], not just hydrophobicity.

Nevertheless, considering the full set of indicators examined in this study, CA correlates more strongly with other soil properties than HI does, and BD emerges as a useful indicator linking hydrophobicity to resilience: as BD (which reflects the status of the soil's porous system [44]); increases, both CA and RS decrease. However, further in-depth studies are required.

CONCLUSIONS

Chilean wetland soils developed pronounced water repellency during drying, especially under severe hydraulic stress. Critically, repellency and pore structure did not behave as independent properties: in the topsoil both recovered within days, whereas in the subsoil repellency persisted and pore volume remained reduced after rewetting. Treating them separately underestimates the change, because it is their joint failure to recover that determines whether the soil can take up and hold water again.

We attribute this coupled irreversibility to these layers having exceeded their all-time maximum dryness level, consistent with a shift from a reversible re-drying regime in the topsoil to a poorly reversible, virgin drying regime in the subsoil, analogous to the transition from recompression to virgin compression in soil mechanics.

The quantity of soil organic matter emerged as a common driver of both hydrophobicity and physical resilience, with total organic carbon and ^{13}C explaining most of the variance in contact angle, and only a secondary, non-independent contribution from compositional indices such as the CHh/COh ratio. Rather than reflecting a direct causal link between hydrophobicity and resilience, this pattern indicates that both processes are co-expressions of the same underlying organic matter gradient, occasionally reinforced by a kinetic protective effect of hydrophobicity against aggregate slaking during rewetting.

The studied wetlands are located in dry regions where stronger desiccation events may become more frequent. Under those conditions, the present results suggest that severe drying can induce substantial repellency in both topsoil and subsoil; beyond the risk of incomplete structural recovery, prolonged hydrophobicity itself may progressively reshape subsoil development by restricting water and gas exchange during extended dry periods, with the main long-term risk concentrated in the subsoil given its comparatively limited recovery capacity relative to the topsoil.

MATERIALS & METHODS

Site selection

A total of 13 individual wetland sites, each contributing one soil profile, were selected across Chile, spanning 38° to 54° S. All sites were situated in semi-arid to arid climatic zones, with water supplied by groundwater, with intermittent surface water inputs (e.g., rivers) in some cases. Soil types included Histosols (n = 4), Fluvisols (n = 6), Cambisols (n = 2), and Gleysols (n = 1) according to [54]. Topsoil organic carbon content differed systematically among these groups, with median values of 33.8% in Histosols, 23.3% in the Gleysol, 11.8% in Fluvisols and 4.1% in Cambisols. The sites therefore span nearly

an order of magnitude in topsoil organic carbon, which allowed the effect of organic carbon content to be examined across a wide range rather than at a single level. Vegetation was predominantly composed of species from the *Cyperaceae* and *Poaceae* families, except at two Histosol sites characterized as *Sphagnum* peatlands (Fig. 1).

Sampling

At each site, a soil pit was excavated (Fig. 1), and samples were collected from the topsoil layer (h1, 0–5 cm) and the subsoil layer immediately above the glacial substrate or water table (h2, approximately 70–75 cm). Ten undisturbed samples were collected from each depth and site following the procedure [55], using stainless steel cylinders (230 cm³; height = 5.6 cm, diameter = 7.2 cm). Each sample was sealed in plastic to prevent moisture loss and transported to the soil physics laboratory. In addition, one disturbed soil sample was collected per site and depth (26 samples in total) for chemical analyses.

Undisturbed Sample Measurements

The 10 undisturbed samples from each depth were slowly saturated by capillary rise over a 7-day period (Fig. 2). Subsequently, samples were equilibrated at successive matric potentials. Samples at -10, -20, -30, and -60 hPa were equilibrated using a sandbox, whereas samples at -150 and -330 hPa were equilibrated in a custom-built pressure chamber manufactured in-house. Figure 2 illustrates this full sequence of saturation, equilibration, stress application, and recovery for both treatments.

Afterward, five samples were subjected to moderate drying stress at -500 hPa for 24 days (mDS), while the remaining five samples were exposed to severe drying stress at -15350 hPa for 48 days (sDS). These periods were determined in preliminary trials as the time required for water loss to cease at each applied tension.

Following the drying treatments, samples underwent a recovery phase by rewetting through capillary rise for 4 days in the moderate drying treatment and 5 days in severely dried treatment, in both cases until water uptake ceased. Subsequently, all samples were again equilibrated at matric potentials of -10, -20, -30, and -60 hPa. At every step of either wetting, drying or re-wetting, water-drop penetration time (WDPT), weight and core volume were measured.

The WDPT test followed [56] A drop of distilled water (approximately 82 µL) was placed at the center of each undisturbed sample surface. The infiltration process was recorded using a Canon EOS Rebel T7 camera until complete penetration of the drop. High-resolution video recordings were then analyzed to determine penetration time (s), measured from the moment the drop contacted the sample surface until no visible trace of water remained.

Water repellency was classified according to [57] as follows: hydrophilic (< 5 s), slightly hydrophobic (5–60 s), strongly hydrophobic (60–600 s), severely hydrophobic (600–3600 s), and extremely hydrophobic (> 3600 s).

In addition, a hydrophobicity index (HI) was calculated from the slope of the line connecting WDPT values measured during stress application and the mean WDPT during the recovery phase, together with the corresponding volumetric water contents, as follows:

$$HI (s) = - \frac{WDPT_{(rec)} - WDPT_{(stress)}}{\theta_{(rec)} - \theta_{(stress)}}$$

1

where $WDPT_{(rec)}$ and $\theta_{(rec)}$ are the water drop penetration time (s) and the volumetric water content ($m^3 m^{-3}$), respectively, averaged over the recovery days (mDS = 4 days, sDS = 5 days). $WDPT_{(stress)}$ and $\theta_{(stress)}$ are the water drop penetration time (s) and the volumetric water content ($m^3 m^{-3}$), respectively, during the application of stress (mDS = -500 hPa, sDS = -15350 hPa). The negative sign in Eq. (1) expresses hydrophobicity loss as an absolute (positive) value, because $WDPT_{(rec)}$ is almost always less than $WDPT_{(stress)}$. HI values were then $\log_{10}$ -transformed for the regression analysis. Physically, HI captures how abruptly water repellency declines as the soil rewets – a measure of the moisture-sensitivity of the hydrophobic surface – rather than the extent of structural recovery. Because the denominator of this index is a difference in volumetric water content, which is itself related to organic carbon content, we verified that HI was not mathematically confounded with soil carbon: across all site–depth–treatment combinations, HI was not significantly correlated with total organic carbon ($r = -0.15$, $p = 0.35$, $n = 44$), and variation in HI was governed more by the change in water drop penetration time (partial $r^2 = 0.75$) than by the change in water content (partial $r^2 = 0.37$).

Vertical deformation were measured using an electronic balance and a caliper gauge with 0.01 mm precision [58]. This allowed the void ratio to be calculated as:

$$VR (m^3 m^{-3}) = \frac{V_f}{V_s} \quad (2)$$

where V_f and V_s are the volumes of pores and soil, respectively. V_s was calculated as the mass of oven-dried soil divided by particle density, which was measured for each site and depth by the pycnometer method [59].

To assess resilience, two indices were developed: a resilience index (RI) and a recovery slope (RS). RI was calculated as follows:

$$RI (-) = \frac{VR_{rec} - VR_{stress}}{VR_{rec}} \quad (3)$$

Where VR_{rec} is the void ratio ($m m^{-3}$) on the last day of recovery (day 4 and day 5 in the moderate and severe treatment, respectively), and VR_{stress} is the void ratio ($m m^{-3}$) during stress application. RI thus expresses the proportion of the final pore volume that represents recovery from the stressed state, with higher values indicating more complete soil structure recovery.

The “Recovery slope” ($RS\ h^{-1}$) was also calculated as a rate. For each core, void ratio was regressed linearly against elapsed time, taking the end of the drying treatment as $t = 0$ and each subsequent recovery measurement at 24-hour intervals; RS is the slope of that regression. The regression therefore used five points in the moderate treatment (stress plus four recovery days) and six in the severe treatment (stress plus five recovery days), rather than a fixed number of days. RS therefore reflects the kinetics of structural recovery, a dimension distinct from the endpoint-based measure captured by RI.

In addition, air conductivity ($kl\ cm\ s^{-1}$) was determined at -60 hPa before and after the application of both stresses, using an airflow meter (Key Instruments, Trevore, USA) capable of measuring kl between 0.1 and 10 $L\ min^{-1}$ and a pressure differential of 0.1 kPa [60].

Finally, the cores were oven-dried at 105°C for 48 h to determine dry soil mass and bulk density (BD), respectively.

Supplementary analyses

The contact angle (CA) was measured on sieved air-dried samples using the sessile drop method (SDM) with a CCD (charge-coupled device)-equipped contact angle microscope (OCA 15, DataPhysics, Filderstadt, Germany) soils. The initial CA was measured immediately after placing a 1 μL drop of deionized water using the SCA20 software (DataPhysics, Filderstadt, Germany). The CA was obtained from drop shape analysis (ellipsoidal fit) and fitted tangents on the left and right sides of the drop, using a linear baseline. The CA was calculated as an average of 6 drops randomly placed on the surface [61].

The cation exchange capacity (CEC), pH, and electrical conductivity (EC), were determined according to [62]. Dry, milled soil was sent to an external laboratory for stable isotope analysis. ^{13}C and ^{15}N natural abundances using isotope ratio mass spectrometry (IRMS-SERCON) according to [63].

Total carbon was determined by placing 200 mg of dried soil sample into a ceramic container lined with ceramic fiber and combusting it in an elemental analyzer (TOC-L CPH / SSM-5000 A, Shimadzu, Japan). To measure total organic carbon (TOC), 150 mg of soil sample was placed into a different ceramic container into which 5 mL of 50% phosphoric acid was added before analysis.

SOM quality was assessed using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) with a Tensor 27 spectrometer (Bruker Optics, Germany). Approximately, 0.5 mg of dry, milled soil sample was mixed with 50 mg of KBr in an agate mortar. Next, 20 mg of the mixture was pressed into a pellet and scanned in the ATR-FTIR spectrometer between 5000 and 220 cm^{-1} . Two pellets were prepared and measured per sample, and their absorbance values at identical wavenumbers were averaged to obtain a single representative spectrum for each site and sampling depth. Spectral noise was subsequently reduced using a Savitzky–Golay smoothing filter using a third-order polynomial and a moving window of 21 data points, preserving the position and shape of the absorption bands while minimizing high-frequency noise.

Hydrophobic and hydrophilic functional groups were identified using an automated peak detection procedure applied to the smoothed spectra. Peak detection was performed independently within the spectral regions corresponding to aliphatic C–H stretching vibrations (3000–2800 cm⁻¹) and carbonyl (C = O) functional groups (1750–1550 cm⁻¹). Local maxima were identified using a minimum peak prominence of 0.005 absorbance units and a minimum separation of 10 spectral points. To ensure a consistent comparison among all sites and sampling depths, peak positions detected across all spectra were pooled and peaks located within 20 cm⁻¹ of each other were merged into a single global reference position. Within the carbonyl window (1750–1550 cm⁻¹), peak detection identified a secondary peak near 1636 cm⁻¹ in addition to the main carbonyl peak (~ 1725 cm⁻¹), potentially reflecting aromatic C = C or residual water contributions. Restricting the window to 1700–1750 cm⁻¹ to isolate the carbonyl signal yielded a CH_h/CO_h index (h: height of absorption band) strongly correlated with the one reported here (r = 0.93, p < 0.01, n = 24), supporting the robustness of this metric to the exact window definition. These global reference peaks were subsequently used for all samples, allowing direct comparison of equivalent absorption bands across the entire dataset.

For each sample, the height of each global reference peak was calculated relative to a local linear baseline constructed from the limits of its corresponding spectral window. The nearest experimental point to each global reference position was used to estimate peak absorbance, and peak height was calculated as the vertical distance between the maximum absorption and its local baseline. Within each spectral region (C–H and C = O), the dominant absorption peak, defined as the peak exhibiting the greatest height relative to its local baseline, was selected to represent the corresponding functional group. A hydrophobicity index was subsequently calculated following an approach similar to that proposed by [64], while incorporating an objective peak detection and peak-matching procedure to ensure consistent identification of equivalent absorption bands among all samples.

The relative hydrophobicity of soil organic matter was estimated as the ratio between the height of the dominant hydrophobic aliphatic C–H band and the height of the dominant hydrophilic carbonyl (C = O) band:

$$CH_h/CO_h = \frac{CH_h}{CO_h}$$

4

where CH_h is the height of the dominant aliphatic C–H absorption band and CO_h is the height of the dominant carbonyl (C = O) absorption band. Similar to the interpretation proposed by [64], higher values of this index indicate a greater relative abundance of hydrophobic aliphatic functional groups with respect to hydrophilic oxygen-containing functional groups [65].

The mean values of the variables used for the regressions and multivariate analyses can be found in S1.

Statistics and Reproducibility

Statistical analyses were performed in Python using *pandas*, *SciPy*, and *statsmodels*, with significance set at $p < 0.05$. For void ratio (VR) and air conductivity (kl), a linear mixed-effects model was fitted separately for each depth (h1, h2), with stage, stress treatment (mDS, sDS), and their interaction as fixed effects and soil core identity as a random intercept. Fixed effects were evaluated using Wald tests. When stage effects were significant within a given stress treatment, pairwise comparisons among stages were performed using paired t-tests with Holm correction. Differences among stages were indicated using uppercase letters. Normality of the paired differences was assessed using the Shapiro-Wilk test; where this assumption was not met, results were confirmed using the non-parametric Wilcoxon signed-rank test, which yielded consistent conclusions for the large majority of comparisons. Additionally, differences between stress treatments (mDS vs. sDS) were evaluated at each stage within each depth using Welch's *t*-tests, with Holm correction for multiple comparisons. Significant differences between stress treatments were indicated using lowercase letters. All tests were two-tailed, with the significance level set at $\alpha = 0.05$. For pairwise comparisons we report the Holm-adjusted *p* value exact *p* values are given except where $p < 0.001$.

Regressions were performed between the calculated variables and the supplementary variables, and the model with the highest R^2 and lowest RMSE was selected. Only significant regressions ($p < 0.05$) are shown, except in Fig. 3 (panels B and D), where linear trends are displayed for illustrative purposes regardless of significance to show the recovery trajectory.

A multivariate principal component analysis (PCA) was performed in R using the FactoMineR and psych packages to determine correlations between the calculated and supplementary variables at the multivariate level. Because the hydrophobicity index (HI), resilience index (RI), electrical conductivity (EC), and the C:N ratio showed poor individual sampling adequacy (measure of sampling adequacy < 0.5), the ordination was performed on the remaining nine variables (CA, RS, TOC, ^{15}N , ^{13}C , CEC, pH, BD, and CHh/COh). Sampling adequacy for this reduced set with a Kaiser-Meyer-Olkin measure of 0.80 was meritorious, and Bartlett's test of sphericity confirmed that the correlation matrix was suitable for ordination (both computed on $n = 47$ complete site-depth-treatment combinations). Chemical and spectroscopic data were unavailable for one site (Pulul 2; see Supplementary Table S1), so all regressions and multivariate analyses involving these variables are based on the remaining twelve sites.

Declarations

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Figures

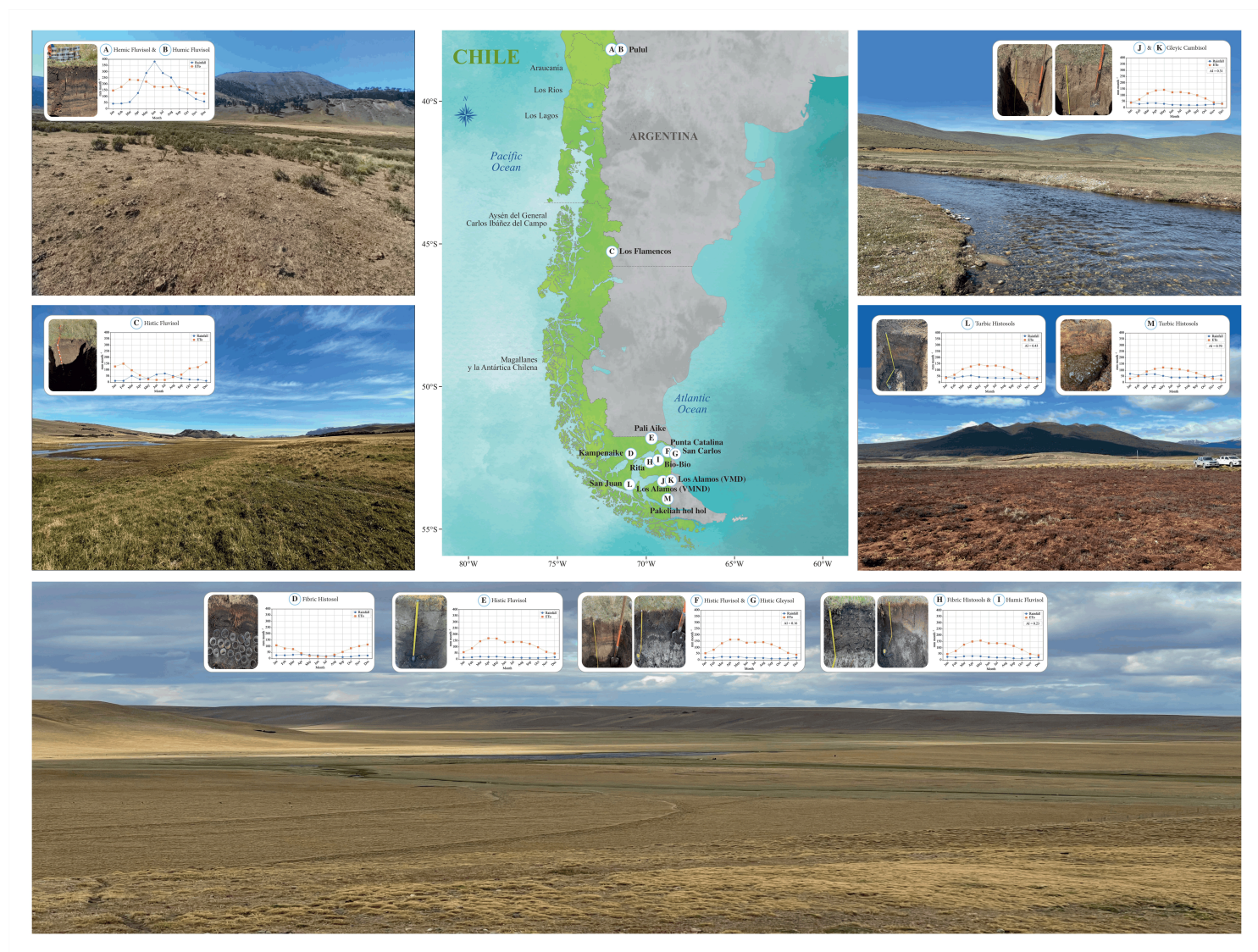


Figure 1

Location, climate, soil profiles and soil types of the 13 wetlands studied. The central map shows the position of each site along the latitudinal gradient (38–54°S); individual soil profiles are identified by the letters A–M and labelled with their WRB soil type. Each inset contains a photograph of the soil profile together with a climodiagram of mean monthly rainfall and reference evapotranspiration (ET₀), both in mm month⁻¹. Where shown, AI is the aridity index, calculated as the ratio between annual precipitation and annual ET₀; values range from 0.16 to 0.70 across the gradient, spanning arid (AI < 0.2), semi-arid

($0.2 \leq AI < 0.5$) conditions. The larger photographs show the representative landscape where each soil profile is located.

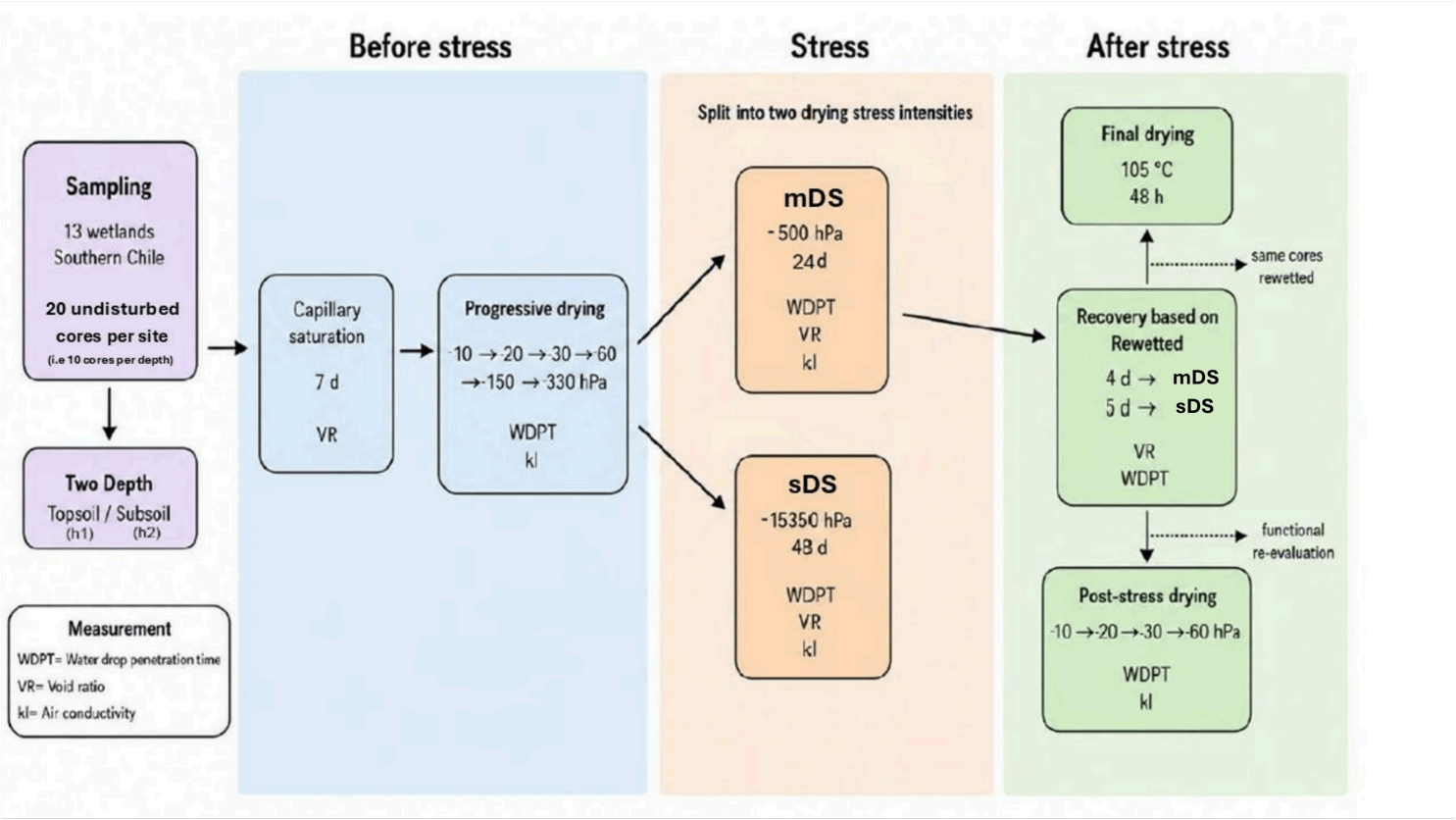


Figure 2

Experimental scheme used to evaluate the water repellency and resilience of wetland soils after application of hydraulic stresses.

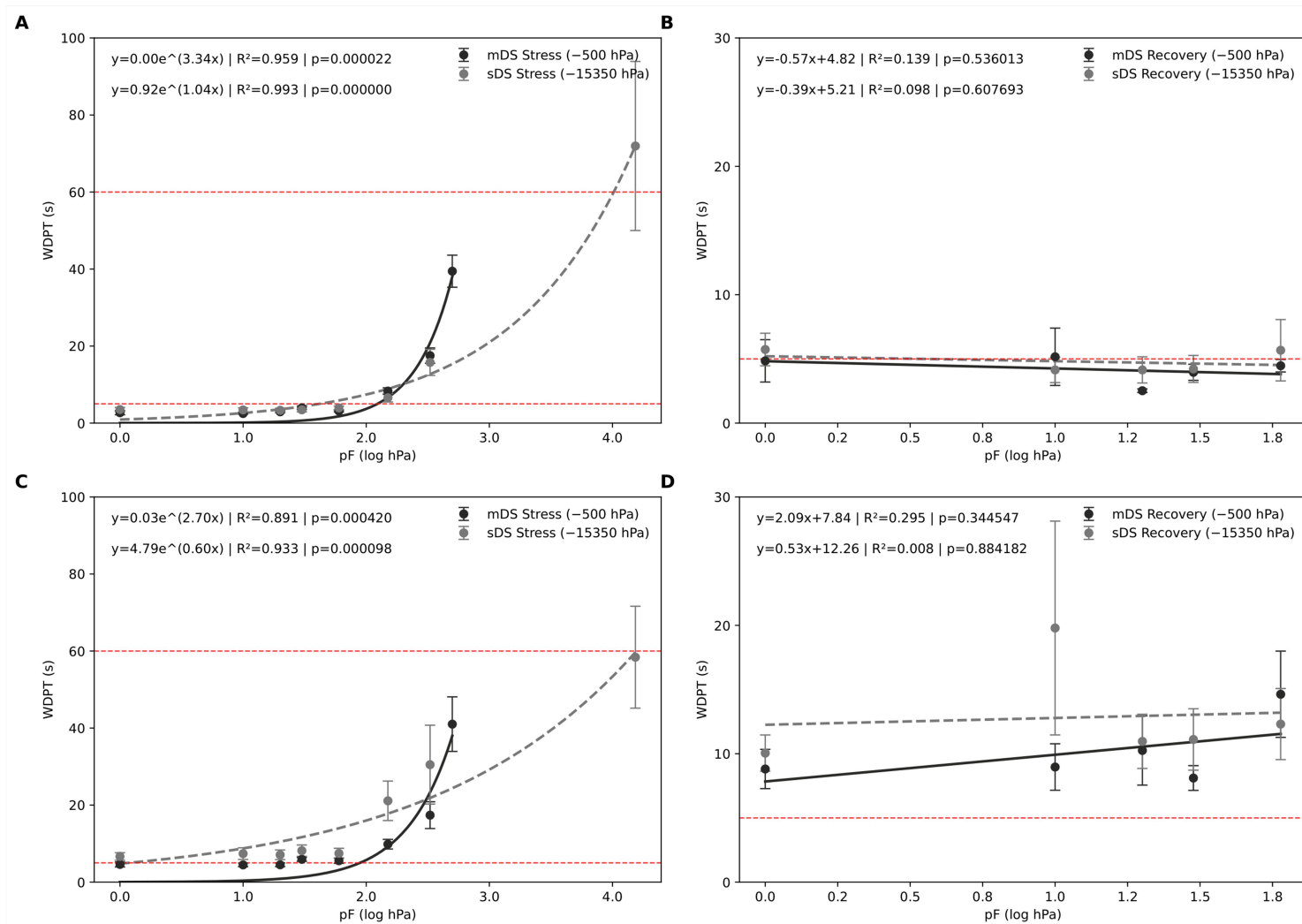


Figure 3

Variation in water drop penetration time tests (s) across the different matrix potential ($pF = \log hPa$). A) represents depth h1 from the start of the experiment until stress is applied (mDS and sDS), and B) represents h1 during the recovery phase from both stresses. C) represents depth h2 from the start of the experiment until stress is applied (mDS and sDS), and D) characterizes h2 during the recovery phase of both stresses. Red dotted lines indicate the boundary between hydrophilic (< 5 s), slightly hydrophobic (5–60 s), and strongly hydrophobic (60–600 s) regions.

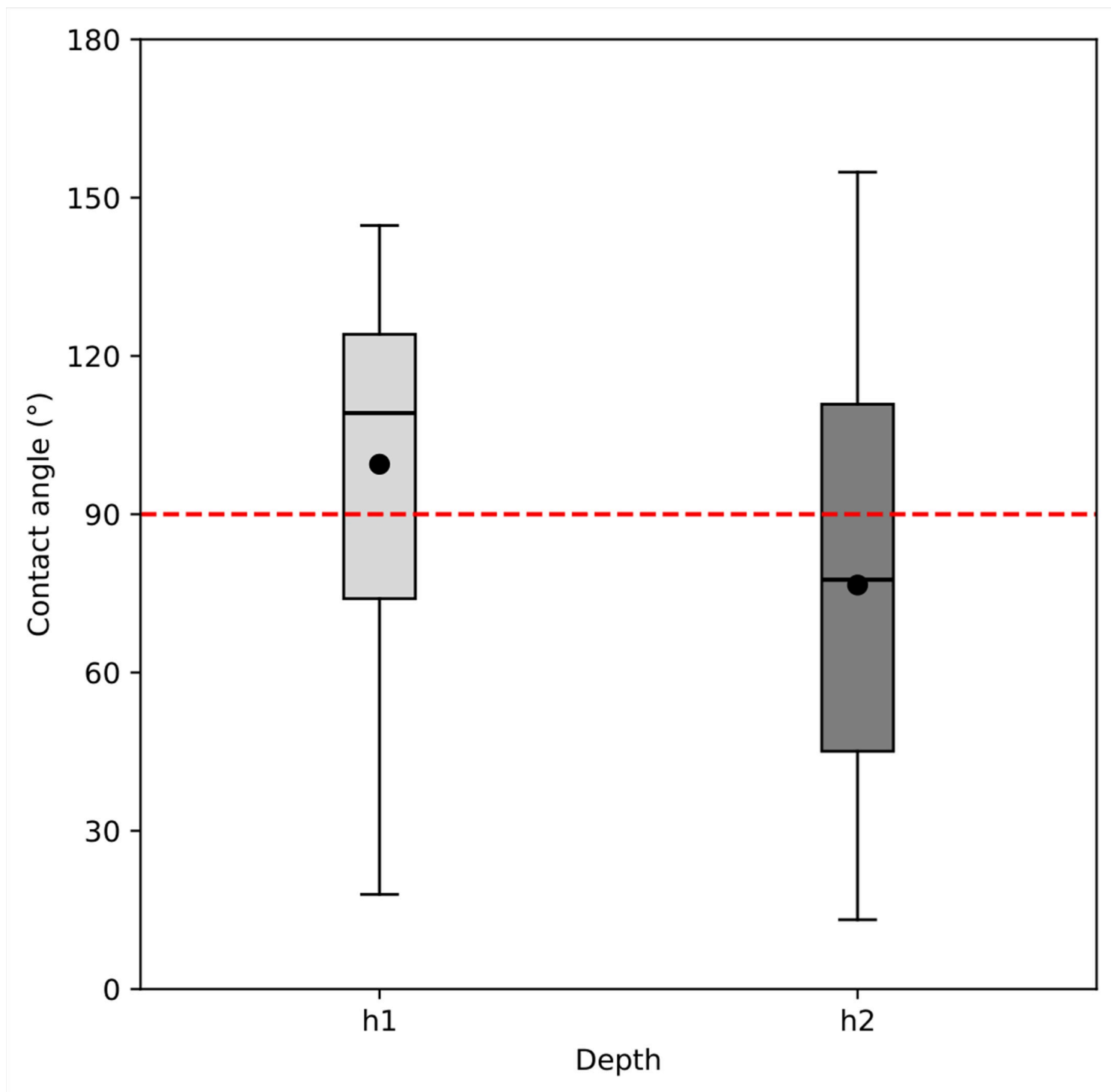


Figure 4

Box plot of the contact angle for depths h1 and h2. The median is marked as a line and the mean as a point. The red dotted line indicates 90°, where the surface changes from being hydrophilic to hydrophobic

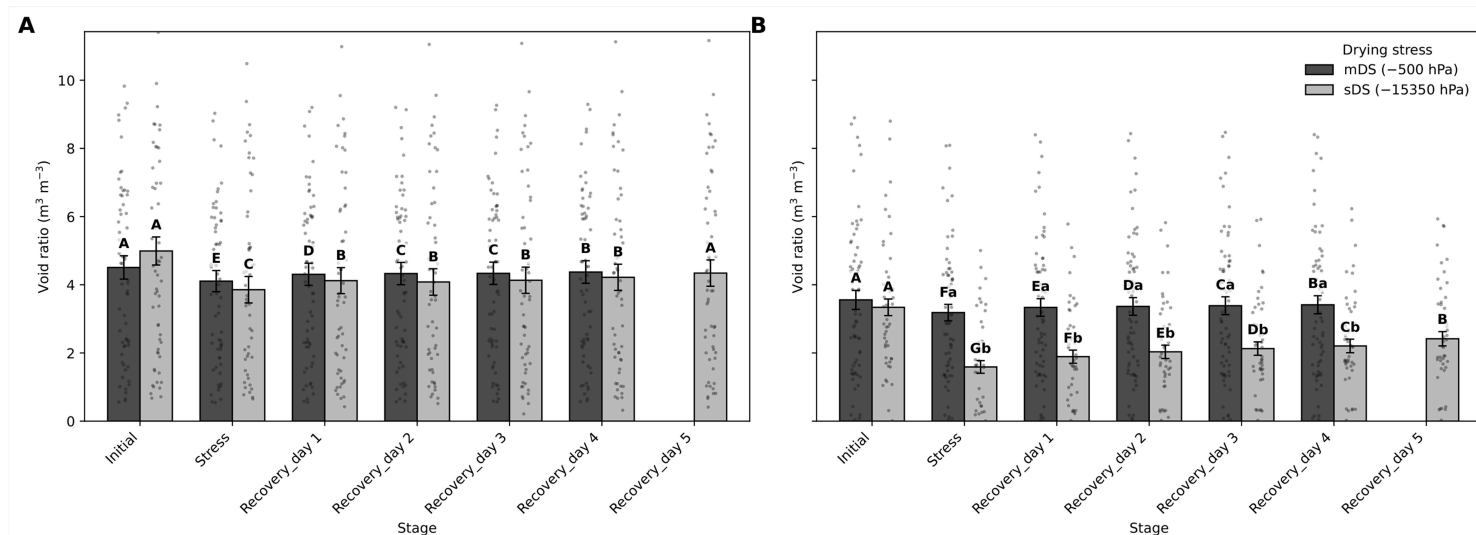


Figure 5

Changes in the void ratio ($\text{m}^3 \text{m}^{-3}$) considering its initial state (saturation before drying), stress (mDS = -500 hPa, sDS = -15350 hPa), and the recovery phase (mDS = 4 days, sDS = 5 days) for depth h1 (A) and depth h2 (B). Capital letters indicate significant differences ($p < 0.05$) between stages for the same stress. Lowercase letters indicate significant differences ($p < 0.05$) between mDS and sDS for the same stage. Bars show the mean and error bars the standard error of the mean (s.e.m.); individual data points are overlaid ($n = 65$ cores per bar).

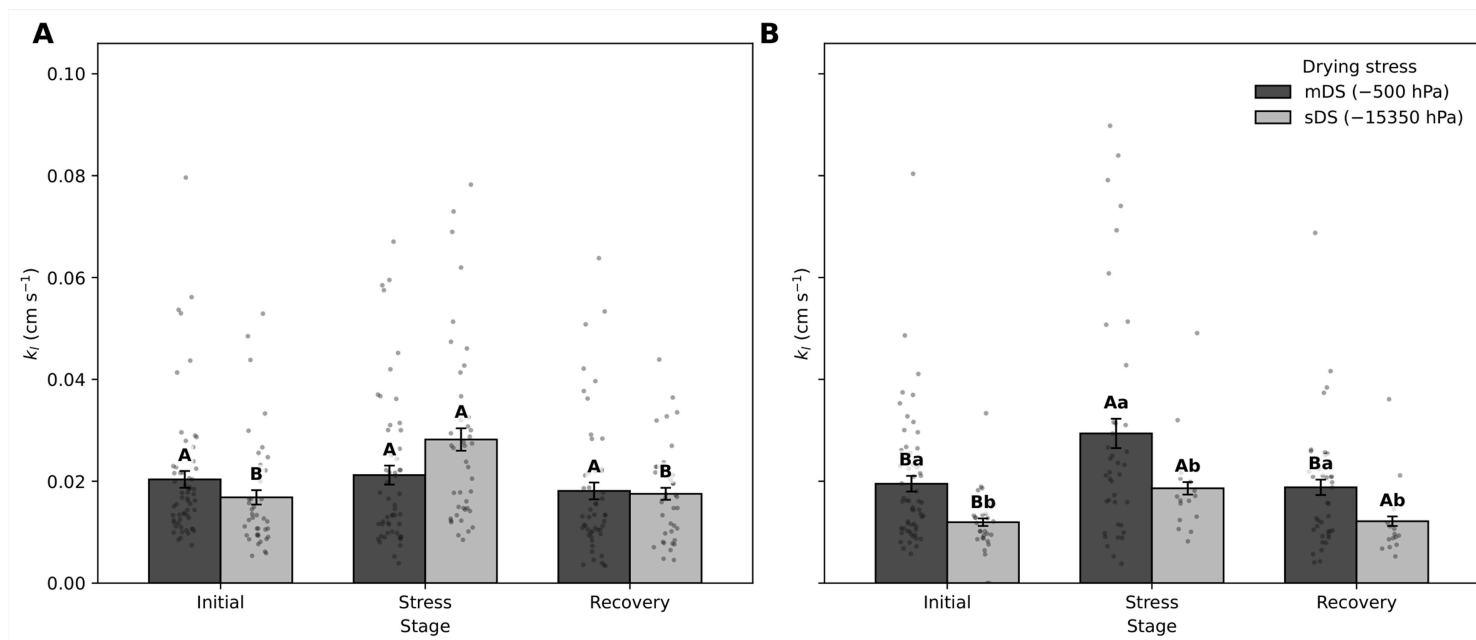


Figure 6

Air conductivity (k_l , cm s^{-1}) measured at -60 hPa before stress application, immediately after stress application, and after the recovery phase (mDS = -500 hPa, sDS = -15350 hPa) for depth h1 (A) and depth h2 (B). Capital letters indicate significant differences (p -value < 0.05) between stages for the same

stress. Lowercase letters indicate significant differences ($p < 0.05$) between mDS and sDS for the same stage. Bars show the mean and error bars the standard error of the mean (s.e.m.); individual data points are overlaid ($n = 65$ cores per bar).

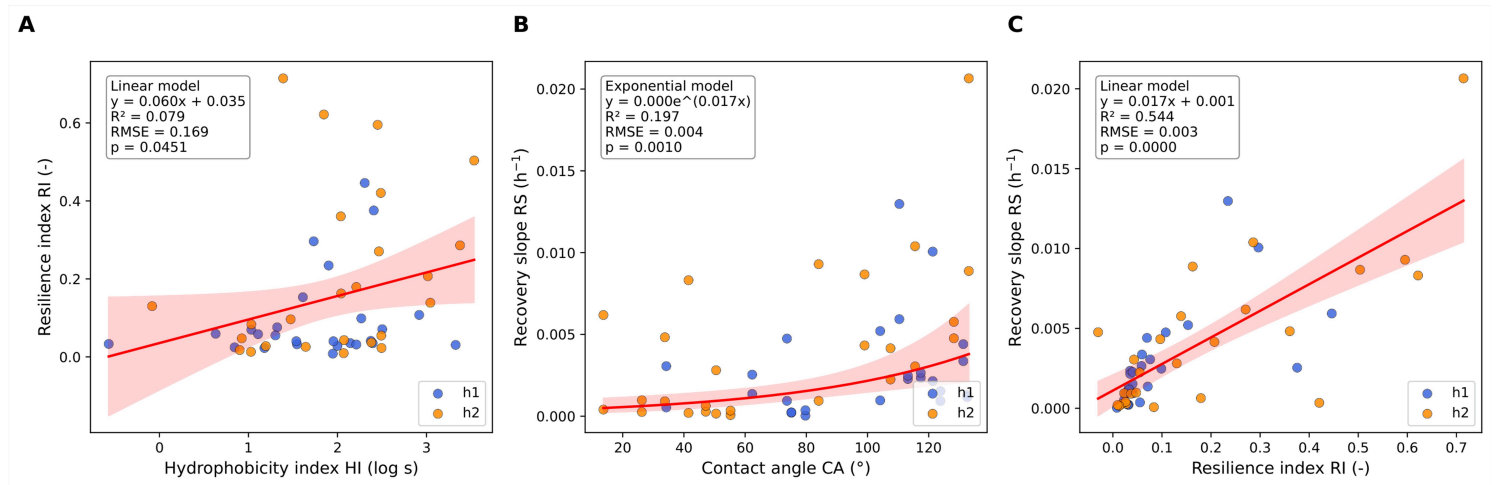


Figure 7

Relationships between soil hydrophobicity indicators and pore-system resilience metrics. (A) Relationship between hydrophobicity index (HI), calculated from the change in WDPT relative to the change in volumetric water content between stress and recovery phases, and resilience index (RI). (B) Relationship between contact angle (CA) and recovery slope (RS). (C) Relationship between RI and RS. RI was calculated as the proportion of void ratio recovered after stress, whereas RS corresponds to the slope of void ratio recovery over time. Red lines represent fitted models and shaded areas indicate the 95% confidence intervals. Points are colored by depth (h1, blue; h2, orange).

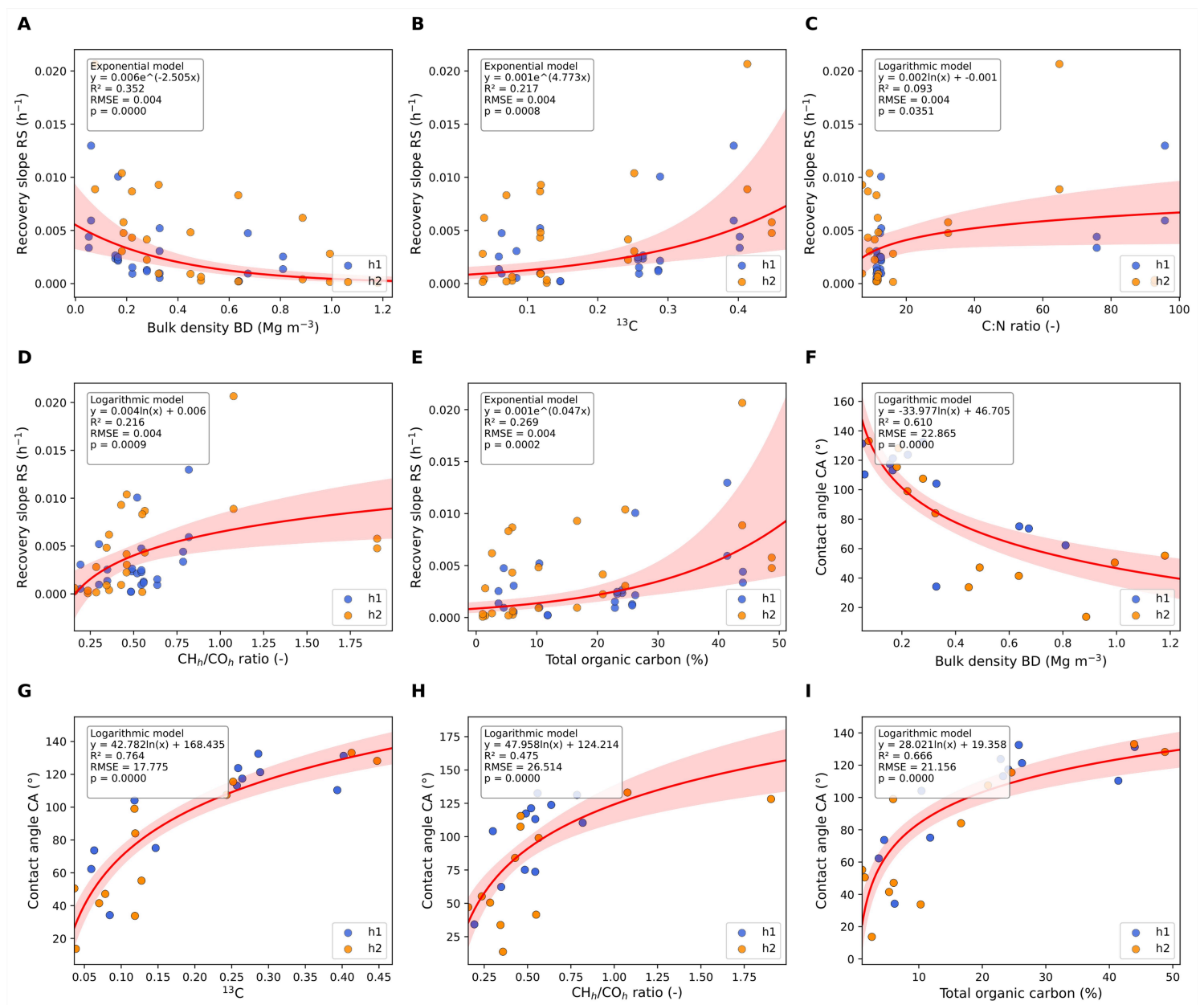


Figure 8

Relationships between selected soil properties with hydrophobicity and pore-system resilience metrics where; A) Bulk density (BD) v/s recovery slope (RS), B) Abundance ^{13}C v/s Recovery slope (RS), C) C:N ratio v/s Recovery slope (RS), D) CH_h/CO_h ratio v/s Recovery slope (RS), E) Total organic carbon (TOC) v/s Recovery slope (RS), F) Bulk density (BD) v/s Contact angle (CA), G) Abundance ^{13}C v/s Contact angle (CA), H) CH_h/CO_h ratio v/s Contact angle (CA), I) Total organic carbon (TOC) v/s Contact angle (CA). Red lines represent the best fitted models (linear, logarithmic, or exponential), and shaded areas indicate the 95% confidence intervals. Contact angle (CA) was used as an indicator of soil surface water repellency, whereas recovery slope (RS) represents the temporal rate of void ratio recovery after stress. Only statistically significant relationships ($p < 0.05$) are shown. Points are colored by depth (h1, blue; h2, orange) in all panels.

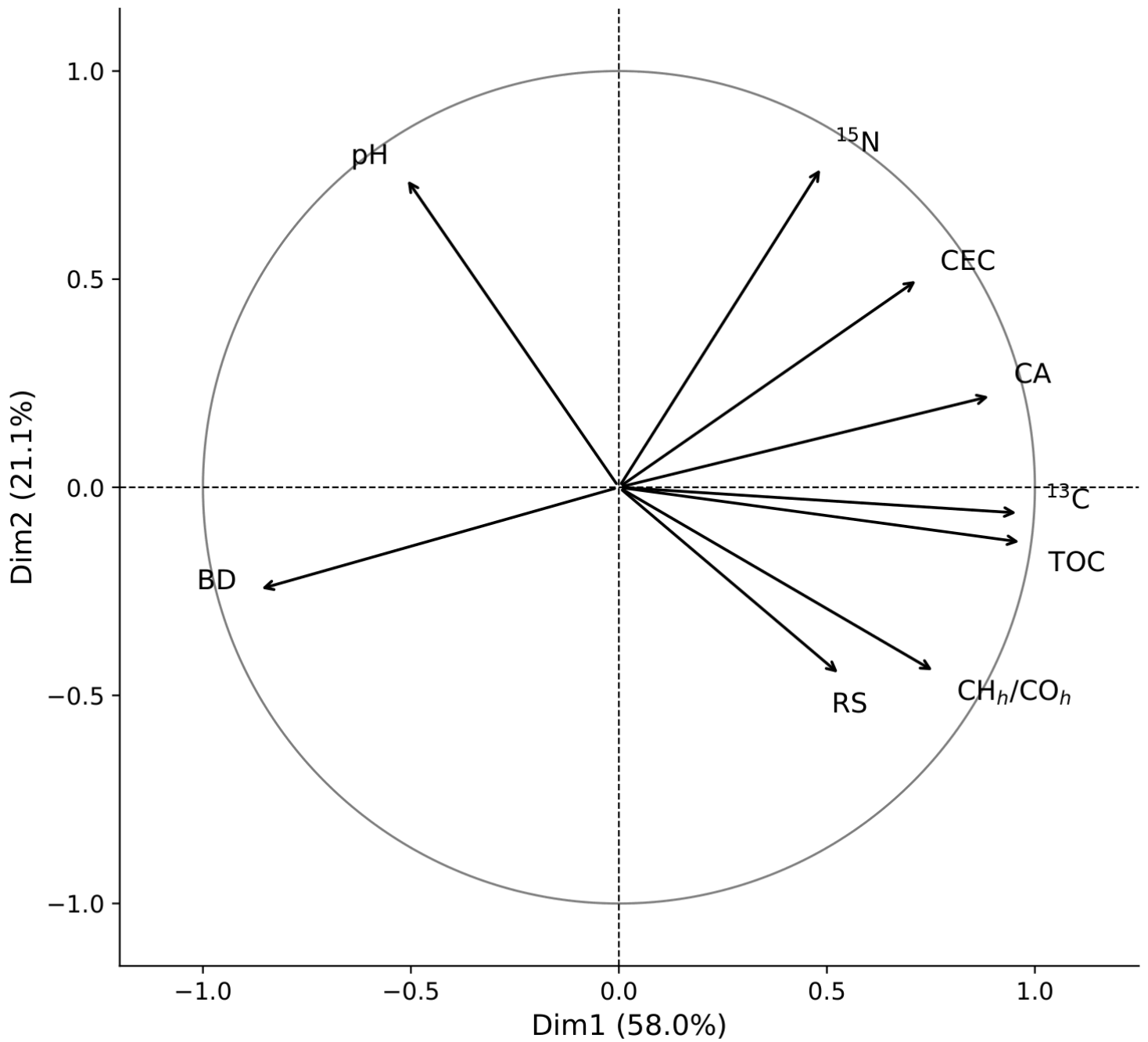


Figure 9

Principal component analysis (PCA) biplot showing the relationships among the hydrophobicity indicator contact angle (CA), the pore-system resilience metric recovery slope (RS), and selected soil physicochemical properties (TOC; ¹⁵N; ¹³C; cation exchange capacity, CEC; pH; bulk density, BD; and the CH_h/CO_h ratio). The hydrophobicity index (HI), resilience index (RI), electrical conductivity (EC), and C:N ratio were excluded from this ordination due to low individual sampling adequacy (see Statistics and Reproducibility). Vector direction indicates variable association, and vector length reflects contribution strength.

Supplementary Files

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- [Supplementary3.0.docx](#)